

超高速激光熔覆 Ni625/WC 复合涂层的耐磨性能

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摘要: 目的 提高高铁制动盘用 24CrNiMo 铸钢的耐磨性和高温性能。方法 在 24CrNiMo 铸钢表面, 通过超高速激光熔覆技术, 制备 Ni625/碳化钨 (WC) 复合涂层, 并设计多层梯度熔覆, 使得 WC 颗粒在涂层中呈均匀分布。通过 X 射线衍射仪 (XRD)、扫描电子显微镜 (SEM) 和透射电子显微镜 (TEM) 等分析涂层的物相组成、微观组织结构和元素分布。分别采用显微硬度计、摩擦磨损试验机、三维形貌仪等测试涂层的硬度、室温及 600 °C 的摩擦系数和耐磨性, 分析涂层的摩擦磨损机理。通过同步热分析仪 (TGA-DSC) 测试涂层的抗高温氧化性能和组织的高温稳定性能。结果 涂层主要由 γ -Ni 固溶体、WC 以及含 W 增强相 W_2C 和 $M_{23}C_6$ 等组成。WC 分布较为均匀, 涂层平均显微硬度达 440HV0.2~610HV0.2, 是基体硬度的 1.25~1.7 倍。在室温条件下, 体积磨损率仅为基体 24CrNiMo 铸钢的 4.2%~20.8%, 摩擦系数略低于基体; 在 600 °C 条件下, 体积磨损率为基体 24CrNiMo 铸钢的 80.1%~180.8%, 摩擦系数高于基体, 且稳定性好, 熔覆涂层显著提高了 24CrNiMo 铸钢基体的耐磨性。磨痕分析表明, 涂层在室温下主要为磨粒磨损, 600 °C 下除了磨粒磨损之外, 还伴随着轻微的氧化磨损, 其中复合涂层 S3 的性能最佳。结论 在以高速强力磨损为主的工况下, Ni625/WC 复合涂层具有优异的耐磨性能和抗高温氧化性能, 球形 WC 颗粒在提高涂层耐磨方面发挥了重要作用。

关键词: 高铁制动盘; 超高速激光熔覆; 摩擦磨损, Ni 基涂层

中图分类号: TH117 **文献标识码:** A **文章编号:** 1001-3660(2023)11-0237-11

DOI: 10.16490/j.cnki.issn.1001-3660.2023.11.018

Wear Resistance of Ultra-high Speed Laser Cladding Ni625/WC Composite Coatings

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ABSTRACT: High-speed train brake disc is one of the important components to ensure the safe and reliable operation of

收稿日期: 2022-10-30; 修订日期: 2023-03-08

Received: 2022-10-30; Revised: 2023-03-08

基金项目: 国家自然科学基金 (51971121, U2106216); 山东省重大创新工程项目 (2019JZZY010303, 2019JZZY010360)

Fund: The National Natural Science Foundation of China (51971121, U2106216); Major-special Science and Technology Projects in Shandong Province (2019JZZY010303, 2019JZZY010360)

引文格式: 李宝程, 崔洪芝, 宋晓杰, 等. 超高速激光熔覆 Ni625/WC 复合涂层的耐磨性能[J]. 表面技术, 2023, 52(11): 237-247.

LI Bao-cheng, CUI Hong-zhi, SONG Xiao-jie, et al. Wear Resistance of Ultra-high Speed Laser Cladding Ni625/WC Composite Coatings[J]. Surface Technology, 2023, 52(11): 237-247.

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high-speed trains. Its main failure form is thermal damage and wear that occurs on or near the friction surface. The use of ultra-high-speed laser melting and other surface strengthening technologies to improve the wear resistance and high-temperature performance of brake discs and other key components is an effective way to ensure the safe operation of high-speed trains. At present, there are many studies on the wear performance of Ni-based WC coatings, but there are relatively few studies on the application of key parts such as brake discs in high-speed trains.

In this paper, Ni625/WC composite coatings was prepared on the surface of 24CrNiMo cast steel for high-speed train brake discs using ultra-high-speed laser melting technology. Since the high specific gravity of WC affected the quality and wear resistance of the coatings, a three-layer gradient coating design was used to improve the distribution of WC particles in the coatings. The phase composition, microstructure and element distribution of the coatings were analyzed by an X-ray diffractometer (XRD), a transmission electron microscope (TEM) and a scanning electron microscope (SEM). The hardness, coefficient of friction and wear resistance of the coatings at room temperature and 600 °C were tested with a microhardness tester, a friction and wear tester and a 3D morphology tester, respectively, and the friction and wear mechanisms of the coatings were analyzed. The high-temperature oxidation resistance and tissue stability of the coatings were investigated with a TGA-DSC simultaneous thermal analyzer.

The results showed that the coatings are well bonded to the substrate, metallurgically, and the total thickness of the coatings was about 300 μm. The coatings were mainly composed of γ -Ni solid solution, WC, W_2C and $M_{23}C_6$ phases. The partial melting and decomposition of WC particles generated different types and multi-scale secondary carbide phases distributed in the intergranular region of the γ -Ni solid solution. In addition, there were lamellar fine eutectic tissues composed of γ -Ni and secondary carbides generated. The hardness distribution of the coatings were relatively uniform, and the average microhardness reached 440HV0.2~610HV0.2, which was 1.25~1.7 times of the matrix hardness (360HV0.2), and the thickness of the heat-affected zone was about 200 μm with a hardness of 410HV0.2. With the increase of WC content, the main wear mechanism at room temperature was abrasive wear, and the volume of wear decreased to 20.8%, 6.8%, 4.4% and 4.2% of the matrix, and the corresponding coefficients of friction were slightly lower than that of the matrix. At 600 °C, it was mainly abrasive wear and slight oxidation wear, and the coefficients of friction were higher than that of the matrix. The high toughness γ -Ni was firmly combined with WC, diffusely distributed secondary carbides and other reinforcing phases, which played the role of wrapping and supporting WC particles, and the multi-scale carbides, mainly WC particles, could effectively resist the indentation of grinding balls, thus reducing plastic deformation and wear. The coatings have good oxidation resistance and tissue stability, which are beneficial to the stability of frictional wear at high temperature. The spherical WC particles play an important role in improving the wear resistance of the coatings.

KEY WORDS: brake discs of high-speed trains; ultra-high-speed laser cladding; frictional wear; Ni-based coating

高铁制动盘是保证高速列车安全可靠运行的重要部件之一。随着高铁的快速发展,对高铁用制动盘提出了更高的性能要求。目前高铁制动盘主要采用圆盘制动方式^[1],国内外制动盘的主流材料是 Cr-Ni-Mo 系铸钢^[2]。在制动过程中,与摩擦副剧烈摩擦,大量机械能转化为热能,局部温度可高达 800 °C,热衰退现象明显。制动盘的主要失效形式是热损伤和磨损^[3],发生在摩擦表面或近表面^[4]。因此,提高制动盘表面的性能,是保障高铁安全运行的关键。

激光熔覆等表面强化技术是提高制动盘等关键件表面耐磨性及高温性能的有效途径^[5-6]。超高速激光熔覆是德国费劳恩霍夫激光技术研究所开发的一种新型激光熔覆技术^[7],熔覆过程中,80%能量被用来熔化粉末,激光扫描速度和生产效率高^[8],而且具有低热影响、低稀释率^[9]和低变形的特点。金属基陶瓷复合涂层兼具陶瓷相的高硬高耐磨以及金属的高

强韧等性能,同时,金属相具有连接和支撑作用,能有效降低凝固开裂倾向。WC 颗粒高熔点、高耐磨、与 Ni 基合金润湿性良好^[10]。目前,激光熔覆碳化钨复合涂层在汽车制动盘领域得到应用,有效地降低磨损和颗粒排放^[11]。未完全熔解的 WC 颗粒具有第二相颗粒强硬化的作用^[12]。Ni625 高温合金具有优良的高温稳定性和抗氧化性能^[13-14],在常温和高温下,通过时效硬化可使得材料具有优异的强韧性能,广泛应用于航空航天、石油化工等行业中。镍基合金在高温下有氧化层产生,显著影响合金的摩擦学性能^[15]。WC 的添加是提高镍基合金涂层摩擦学性能的有效途径^[16]。在高温下,碳化物相保持不变,促进了热稳定性,并且得到比镍基合金更好的耐高温磨损性能^[17-18]。

目前,对 Ni 基 WC 涂层的磨损性能研究较多,但在高铁制动盘等关键件的应用研究相对较少。本文采用超高速激光熔覆技术在制动盘用钢表面制备

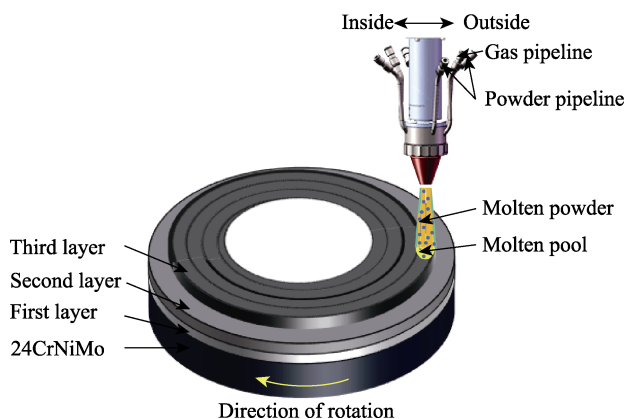


图2 超高速激光熔覆示意图
Fig.2 Schematic diagram of ultra high-speed laser cladding

1.3 测试方法

通过线切割制备样品（10 mm×10 mm），然后用SiC砂纸打磨，抛光绒布抛光，酒精清洗干燥，用于测试。使用D/MAX-2500PC型X射线衍射仪（Rigaku, Japan）鉴定相组成，采用Cu靶[40 kV, 100 mA, 4 (°)/min, 20°~100°]。使用FEI-Nano SEM 450型扫描电子显微镜（SEM）观察样品的微观组织结构。采用Thermo Fisher Scientific Talos F200X G2型高分辨率透射电子显微镜（HRTEM）对涂层的晶体结构进行表征。采用HVS-1000维氏硬度计测试涂层截面硬度（15 s, 载荷为1.96 N, 间距为50 μm, 每深度区域间隔200 μm, 测试5次取平均值）。采用TGA/DSC1型同步热分析仪进行热分析测试（升温速度10 °C/min, 200~1000 °C）。

采用Rect MFT-5000多功能磨损试验机进行干滑动往复摩擦（载荷30 N, 摩擦速率10 mm/s, 摩擦时间30 min）测试试样的室温耐磨性，对磨材料为Al₂O₃陶瓷球（硬度≥16 GPa, 直径为9.5 mm）。采用THT07-135型高温摩擦磨损试验机测试涂层的高温耐磨性（6 mm Al₂O₃陶瓷球, 600 °C, 载荷为30 N, 摩擦速率为10 mm/s, 摩擦时间为30 min）。使用Bruker Contour GT-K1型三维轮廓仪测试体积损失和磨损形貌。

2 结果与讨论

2.1 熔覆层相组成

Ni625/WC复合涂层的X射线衍射图谱见图3。可以看出，Ni625/WC复合涂层的主要物相是γ-Ni固溶体相、WC以及含W增强相W₂C和M₂₃C₆等二次碳化物相。WC相来源于原料，含W增强相来自WC颗粒部分熔化分解为自由W原子和C原子后，与Ni625合金中的Cr、Mo、Fe等金属元素结合生成

的不同类型二次碳化物相。随着WC含量的增加，WC相及含W增强相的衍射峰逐渐增强。

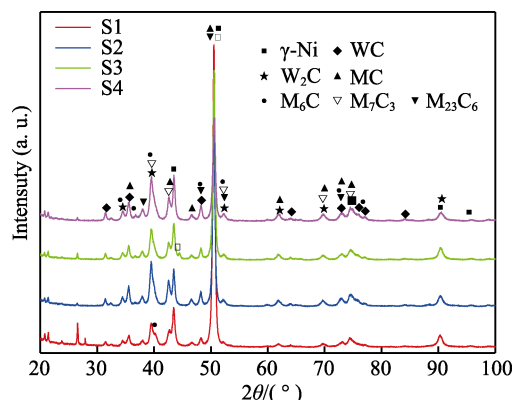


图3 Ni625/WC复合涂层的XRD图谱
Fig.3 XRD patterns of Ni625/WC composite coatings

2.2 熔覆层截面微观形貌

涂层的截面扫描形貌如图4所示。可以看出，涂层与基体、涂层与涂层之间结合良好，为冶金结合，界面处为一薄层平面晶^[19]。涂层的厚度较为均匀，约为0.3 mm。各涂层中WC颗粒形状保持良好，且出现在第一层过渡层中，提高了过渡层的耐磨性。从析出相的形状和XRD结果可以推断，灰色相为γ-Ni固溶体相，白色球状相是未完全分解的WC颗粒，环绕在WC颗粒周围的是W₂C、M₂₃C₆等二次碳化物。

超高速激光熔覆时，在热源作用下，熔池温度超过WC的熔点，但冷却速率快，远远高于传统激光熔覆^[20]，导致WC颗粒表面部分分解。随着WC含量的增加，生成的二次碳化物的含量越高^[21]。冷却时，未完全熔化的WC颗粒先凝固，促进熔点低Ni625粉末形核^[22]，细化晶粒，二次碳化物相分布在γ-Ni固溶体的晶间区域。此外，还有由γ-Ni和二次碳化物组成的片状细小的共晶组织生成，涂层的强韧性得到提高^[23]。S3涂层的共晶组织最为细小，S4涂层的共晶组织中的碳化物相，逐渐长大为细颗粒状。另外，WC颗粒也可以起到第二相颗粒强化的作用。

图5a为S3涂层的TEM亮场图像，其中白色相是γ-Ni基固溶体相，灰色相是富W碳化物相。元素分布图显示，有纳米级二次碳化物的存在。分解产生的自由W和C原子，扩散到周围γ-Ni中，与Cr、Mo等混合熔^[24]较负的元素形成多种碳化物析出相，改变了γ-Ni相成分，不同的析出相互互连接，分布在枝晶间区域^[25]。图5b为γ-Ni晶粒的HRTEM放大图像，图5c为电子衍射图，基体晶粒沿[001]轴为FCC结构。图5d为M₂₃C₆晶粒的HRTEM放大图像，图5e为选区电子衍射图，晶粒沿[111]轴为FCC结构。

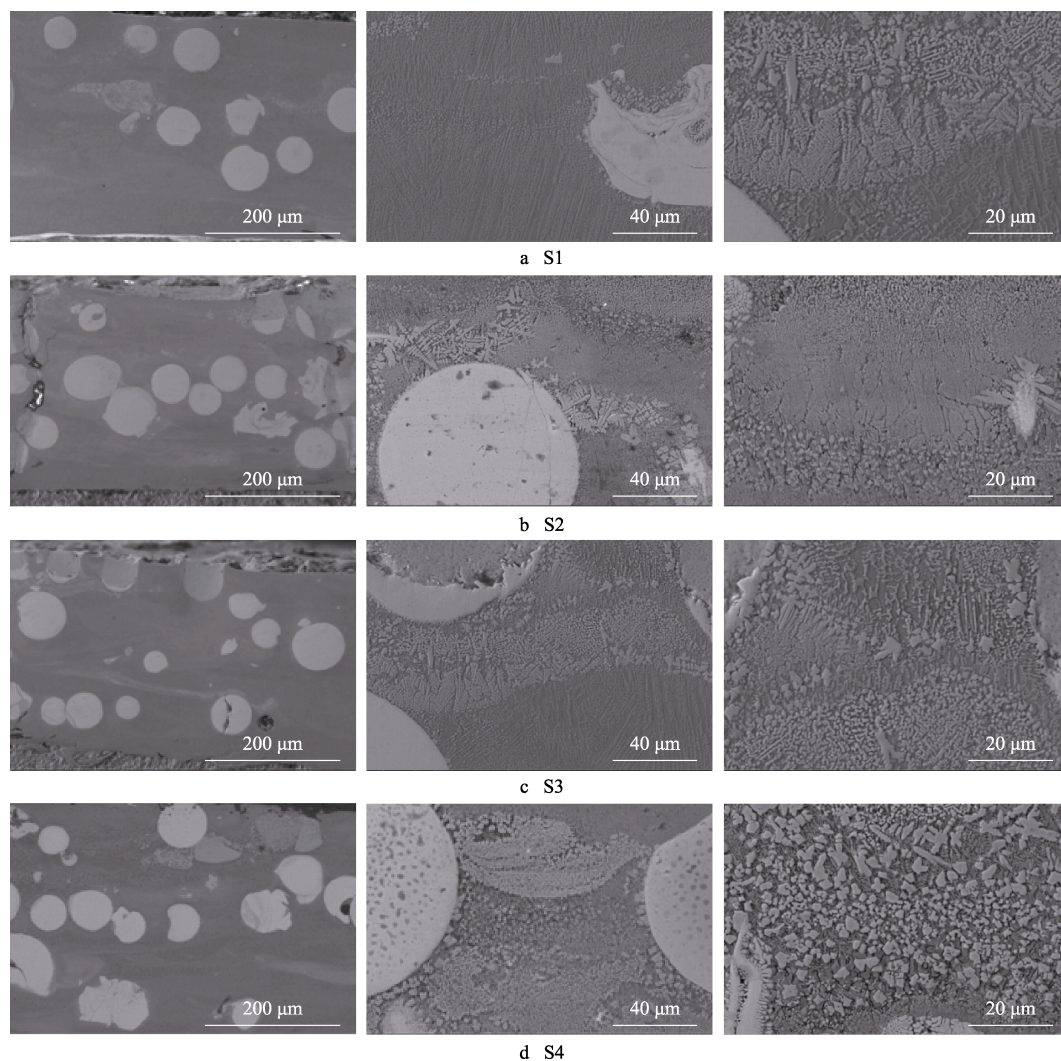


图 4 各试样的截面 SEM 形貌
Fig.4 Cross-sectional SEM morphologies of each sample

由于超高速激光熔覆层的快速冷却, W 原子的扩散速率远远低于 C 原子, 在 γ -Ni 基固溶体相中形成多尺度、高度致密的二次碳化物相, 有纳米级层片状共晶组织、点状沉淀相、块状沉淀相, 有助于提高涂层力学性能^[26]。最终在涂层中形成一种核壳结构, WC 颗粒-二次碳化物相- γ -Ni 固溶体相, 硬质相-中间相-软质相三相结合, 共同提高涂层的耐磨性。

2.3 显微硬度分析

图 6 为 Ni625/WC 复合涂层的显微硬度, 测量过程中避开 WC 颗粒。随着 WC 含量的增加, Ni625/WC 复合涂层的平均显微硬度为 445HV0.2~610HV0.2, 基体硬度为 355HV0.2。热影响区 (HAZ) 的厚度约为 200 μm 。在超高速激光熔覆过程中, 80% 的能量作用于粉末, 对基体的热输入小, 淬火效应小, 导致热影响区小^[27], 且硬度提升较小, 其硬度最高为 410HV0.2。超高速激光熔覆时, 线速度高, 且冷却速

率快, WC 颗粒促进形核, 细化晶粒, 产生大的晶格畸变, 有效阻碍位错滑移, 使得涂层硬度提高。多尺度的二次碳化物引起的第二相强化是提高涂层显微硬度的重要因素, 但降低了涂层的韧性。

2.4 熔覆层摩擦磨损性能分析

2.4.1 室温耐磨性分析

图 7a 为室温下的摩擦系数曲线, 可以观察到基体和涂层的磨合和稳定磨损阶段。磨痕表面周期性局部断裂和磨屑在磨损表面的积累和清除^[28]是造成摩擦系数曲线波动的主要原因。基体的摩擦系数稳定在 0.42, 而涂层的摩擦系数均略低于基体的摩擦系数^[29], 分别为 0.40、0.37、0.38、0.41, 先减小、后增加。随 WC 含量的增加, 涂层接触面中的 WC 颗粒凸起越多, 粗糙度增加, 摩擦系数增加。从图 7b 可以看出, 基体的磨损量最大, Ni625/WC 复合涂层的磨损量随 WC 含量的增加逐渐降低, 仅为基体的 4.2%~20.8%, 耐磨性得到极大提高。

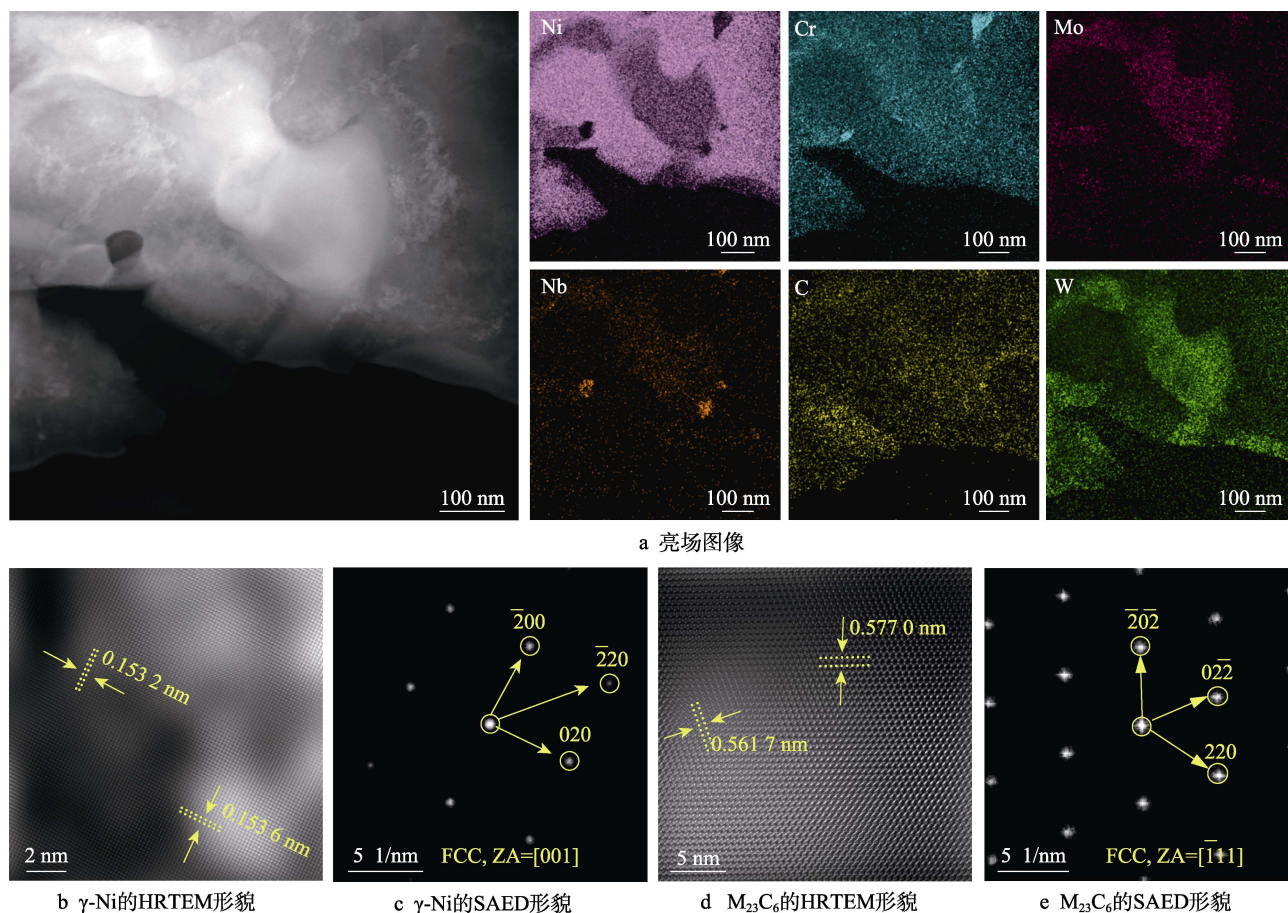


图5 S3涂层的TEM图

Fig.5 TEM images of S3 coatings: (a) bright-field image; (b)(c) HRTEM image and SEAD-pattern of γ -Ni matrix; (d)(e) HRTEM image and SEAD-pattern of $M_{23}C_6$

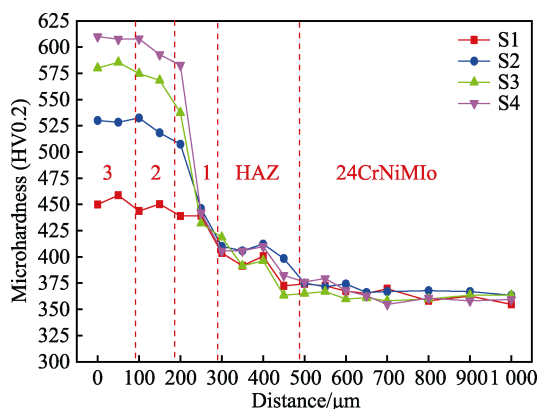


图6 Ni625/WC复合涂层的显微硬度

Fig.6 Microhardness of Ni625/WC composite coatings

室温摩擦磨损条件下的磨痕形貌如图8所示。可以看出,基体的磨痕表面比较光滑,有明显的犁沟和塑性变形,为磨粒磨损机制。涂层的磨损机制主要是磨粒磨损,随着WC含量的增加,磨痕逐渐变浅和变窄,除了有明显的犁沟和剥落坑外,还有过大的局部应力使磨屑堆积在WC附近,硬质磨粒来源于剥落的二次碳化物。以WC颗粒为主的多尺度碳化物能有效抵抗 Al_2O_3 磨球的压入,从而减少塑性变形和磨损。

部分WC颗粒在磨球的压入下破碎,未发现剥落,说明在干式滑动摩擦磨损试验所带来的正压和剪应力作用下,WC能更好地传递和承载载荷。高韧性的 γ -Ni与WC、弥散分布的二次碳化物等牢固结合,起着包裹与支撑WC颗粒的作用,高耐磨的WC颗粒能够降低涂层磨损程度,使涂层表现出优异的耐磨损性能。

2.4.2 高温耐磨性分析

图9a为600℃条件下的摩擦系数曲线。可以看出,基体的摩擦系数在室温下为0.42,在600℃下降到0.31,之后又逐渐降低至0.23,热衰退现象明显。涂层的摩擦系数为0.38、0.37、0.34、0.33,摩擦系数曲线波动较基体和室温大,与摩擦过程中氧化膜的生成和破坏有关,而且氧化膜的生成,具有减磨作用,导致摩擦系数的相较室温时略有降低。从图9b中可以看出,基体的磨损量较少,主要是由于摩擦系数降低引起的。此外,涂层S3的磨损量最少。

从图10可以看出,基体的磨痕较为光滑,有浅的犁沟,还有剥落坑。从三维形貌图中可以发现,未磨损表面变得粗糙,主要是氧化产生的氧化膜导致,基体主要磨损机制是氧化磨损和轻微的黏着磨损。涂层的磨痕较室温光滑,有细小的犁沟,化学成分见表3。

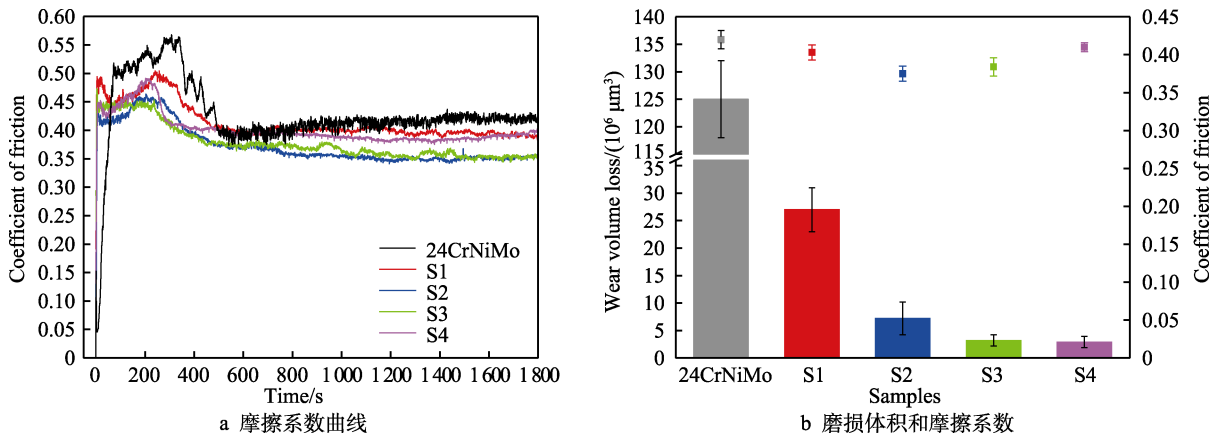


图 7 Ni625/WC 复合涂层在室温下的摩擦磨损
Fig.7 Frictional wear of Ni625/WC composite coatings at room temperature: a) friction coefficient curve; b) Wear volume and friction coefficient

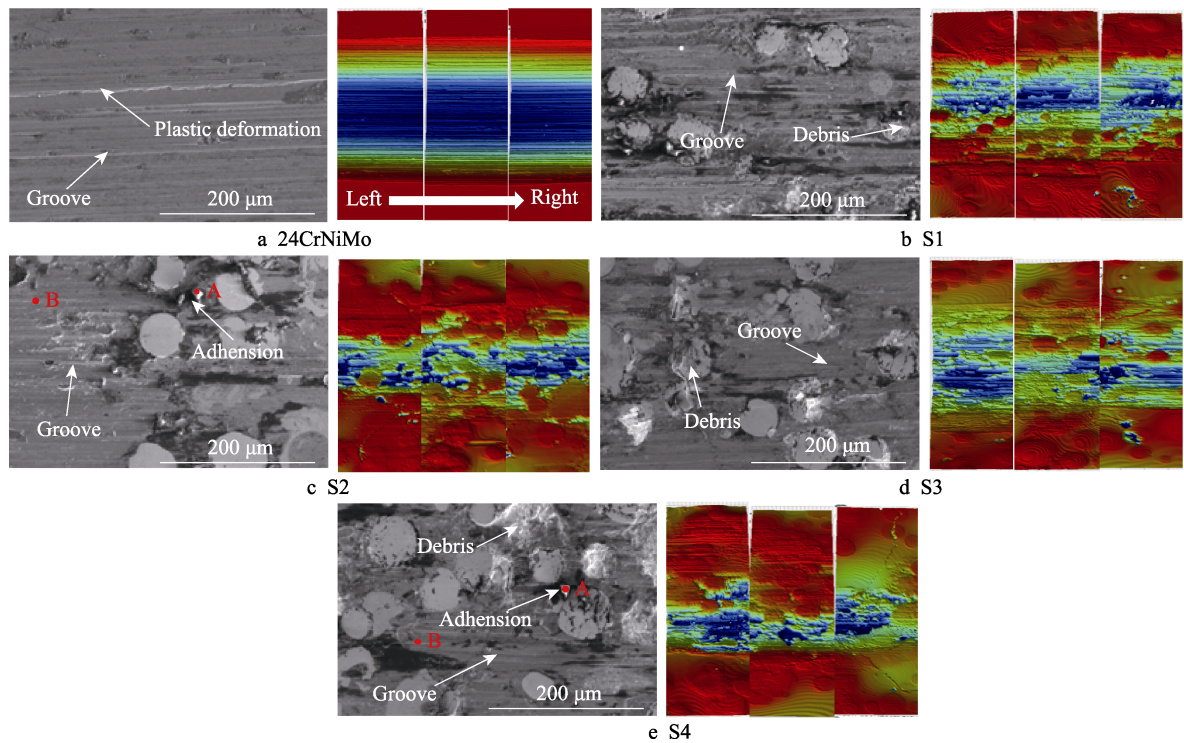


图 8 Ni625/WC 复合涂层在室温下的磨痕 SEM 和三维形貌

Fig.8 SEM images and 3D morphology of worn surfaces of Ni625/WC composite coatings at room temperature

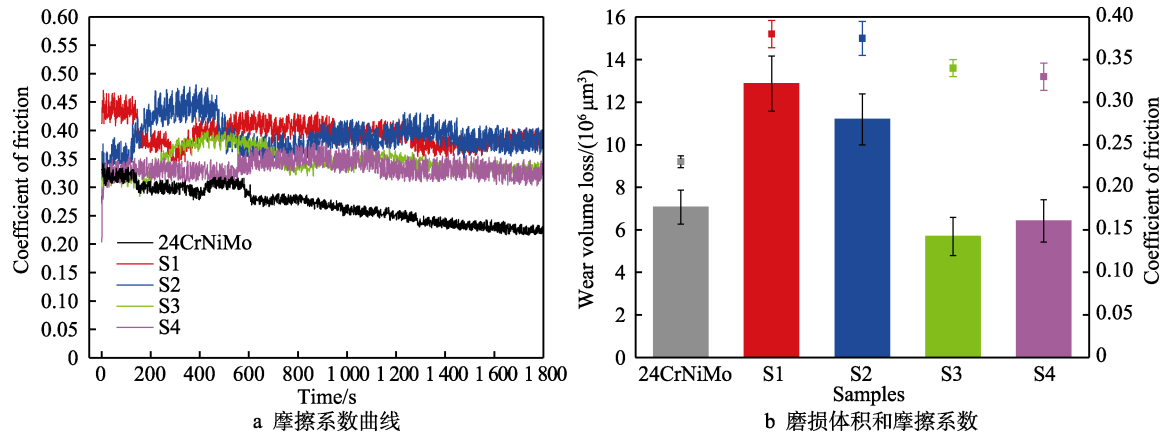


图 9 Ni625/WC 复合涂层在 600 °C 下的摩擦磨损
Fig.9 Frictional wear of Ni625/WC composite coatings at 600 °C: a) friction coefficient curve; b) Wear volume and coefficient friction

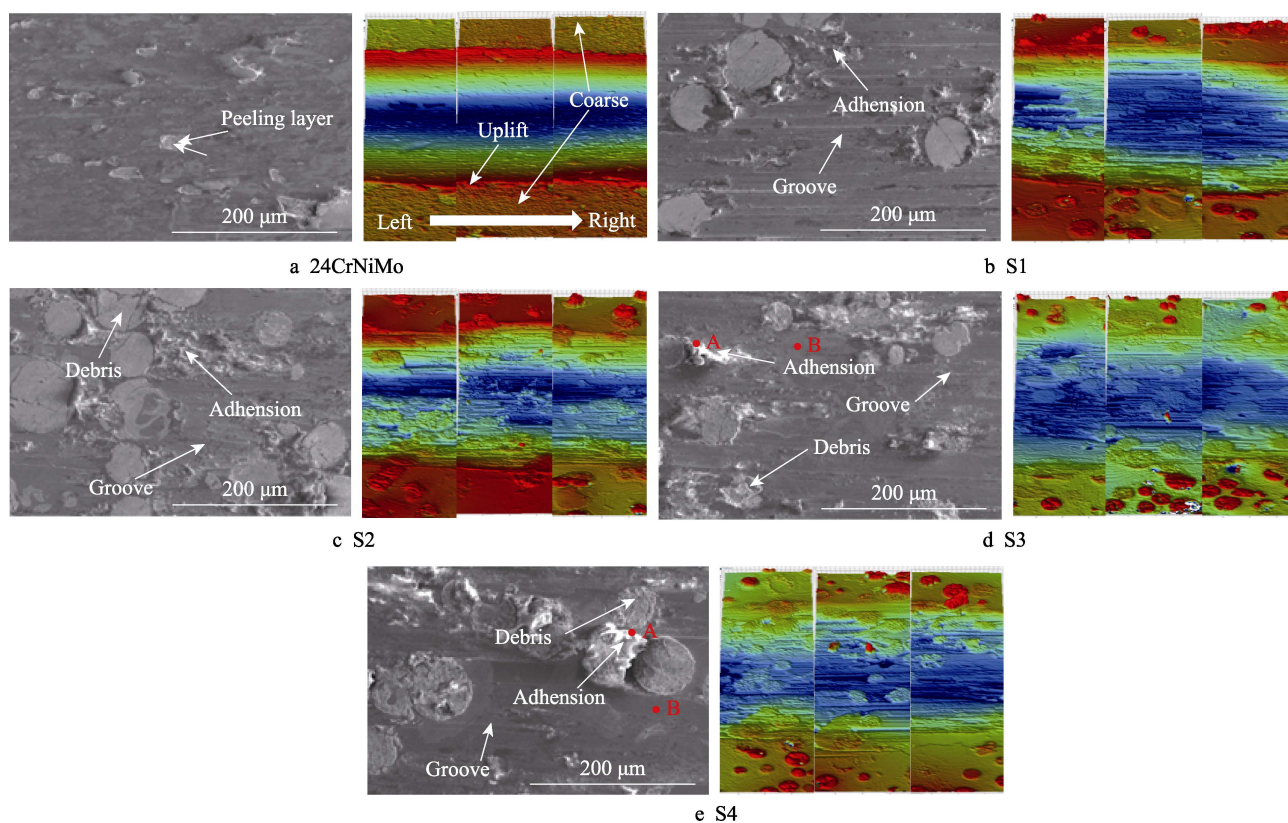


图 10 Ni625/WC 复合涂层在 600 °C 下的磨痕 SEM 和三维形貌
Fig.10 SEM images and 3D morphology of worn surfaces of Ni625/WC composite coatings at 600 °C

表 3 图 8 和图 10 中不同位置的化学成分
Tab.3 Chemical composition of different positions in Fig.8 and Fig. 10

Elements	at. %							
	S2		S4		S3(600 °C)		S4(600 °C)	
	A	B	A	B	A	B	A	B
C	9.45	35.71	28.58	56.68	13.62	58.85	24.19	52.61
O	68.43	13.20	54.53	3.69	60.23	3.80	57.84	11.47
Al	16.89	0.93	9.60	0.10	19.75	0.32	9.67	0.68
Cr	0.66	12.77	1.17	9.14	0.33	5.15	0.40	5.19
Fe	0.14	1.14	0.11	0.80	2.06	6.57	2.44	10.92
Ni	1.59	30.65	3.27	22.80	2.73	12.90	2.53	9.22
Nb	0.00	0.80	0.01	0.96	0.04	0.00	0.06	0.10
Mo	0.14	2.19	0.27	3.12	0.25	1.88	0.22	0.76
W	2.69	2.61	2.47	2.71	1.00	10.54	2.66	9.04

富 Cr、Ni 元素，主要是 γ -Ni 固溶体。此外，富 O 元素，为 Cr 和 Ni 的氧化物，即磨损表面在室温及 600 °C 下均发生了氧化现象。另外还有磨损产物堆积在 WC 颗粒附近，富 O、Al 元素，主要为对磨副 Al_2O_3 磨屑，磨损机制为磨粒磨损和轻微的氧化磨损。

磨损产物的 SEM 形貌如图 11 所示。亮白色颗粒为富 W 的碳化物颗粒，灰色相为剥落的 γ -Ni 固溶体和 Al_2O_3 磨屑。磨屑主要呈细小颗粒状和高温及挤压作用下发生氧化聚集长大的层片状。相较于室温，600 °C 下层片状的磨屑增多，有利于磨屑的排除，降低摩擦系数的不稳定性。氧化物的摩擦系数较小^[29]，同时磨痕较为光滑，粗糙度降低，导致其摩擦系数降低。磨痕处的 WC 颗粒保持良好，在高温下 Ni625/WC 复合涂层依然保持了良好的耐磨性。

2.5 熔覆层同步热分析测试

图 12a 为热重 (TG) 曲线，在 200~550 °C，基体和涂层增重趋势相近，550 °C 时，基体的氧化质量增加加快，而涂层的质量增加速率均在 700 °C 时开始增加，基体的质量增量大于涂层，涂层的抗氧化性能优于基体，有利于保持摩擦系数的稳定性。涂层 S1、S2 的质量增量曲线相近，涂层 S3 和 S4 的质量增量曲线相近。从图 12b 的 DSC 曲线可以看出，涂层和基体一直处于氧化吸热状态。与基体相比，涂层没有吸热或放热峰出现，说明在 200~1 000 °C 未发生相变，即涂层具有良好的高温稳定性。在高温下，Ni625/WC 复合涂层能够保持良好的强韧性，有利于高温下摩擦的稳定性。

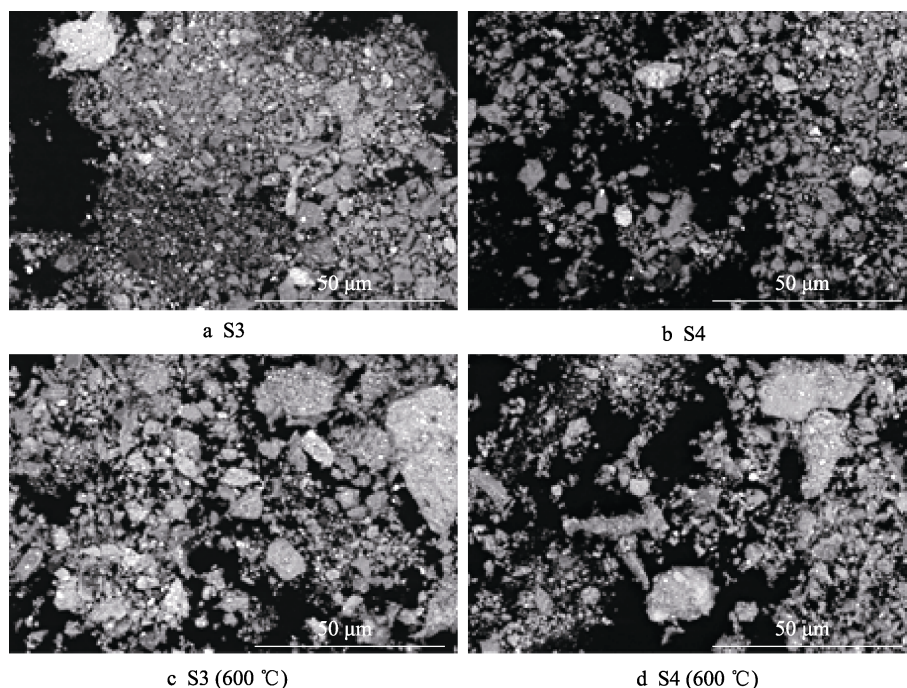


图 11 Ni625/WC 复合涂层摩擦磨损产生的磨屑 SEM-BSE 形貌

Fig.11 SEM-BSE images of abrasive dust of Ni625/WC composite coatings of frictional wear

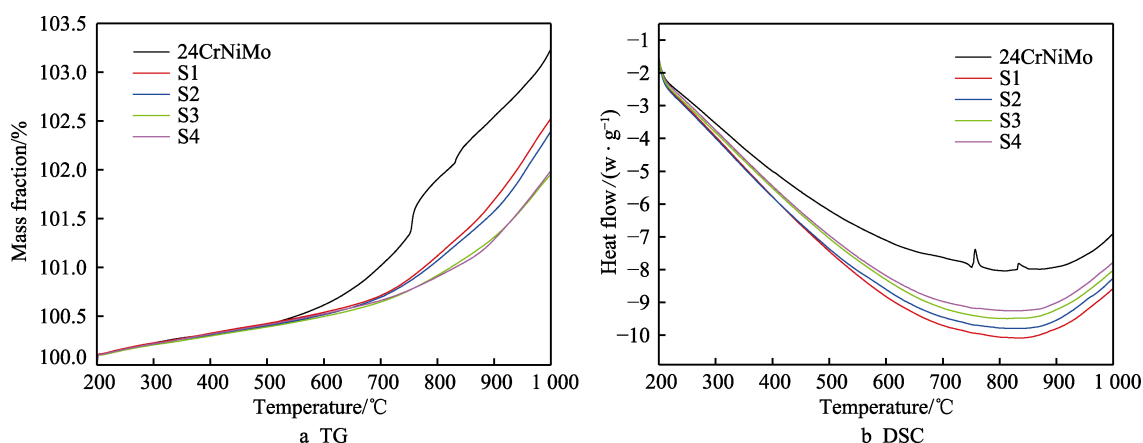


图 12 Ni625/WC 复合涂层的热分析试验

Fig.12 Thermal analysis experiments of Ni625/WC composite coatings

3 结论

采用超高速激光熔覆技术在 24CrNiMo 铸钢表面制备了 Ni625/WC 三层梯度复合涂层, 并研究了其显微组织和耐磨损、抗高温氧化性能等。主要结论如下:

1) Ni625/WC 复合涂层具有复杂的微观结构, WC 颗粒加入后, 在激光热源的作用下部分分解, 形成了 W_2C 和 $M_{23}C_6$ 等二次碳化物相, 分布在 γ -Ni 固溶体晶间位置。

2) Ni625/WC 复合涂层中 WC 颗粒与多尺度的二次碳化物共存, 协同提高涂层的硬度和耐磨性, 涂层摩擦系数稳定。室温下涂层的磨损机制主要是磨粒磨损, 600 °C 下涂层的磨损机制除了磨粒磨损, 还出现轻微的氧化磨损。

3) Ni625/WC 复合涂层具有良好的高温稳定性及抗高温氧化性能, 有利于提高高温耐磨性能。

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